NASA TN D-7177

$N73-18536$

EFFECT OF DIFFUSIONAL CREEP ON PARTICLE MORPHOLOGY OF POLYCRYSTALLINE ALLOYS STRENGTHENED BY SECOND-PHASE PARTICLES

by John D. Whittenberger and Donald R. Behrendt

Lewis Research Center

Cleveland, Ohio 44135

1. Report No. NASA TN D-7177	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle EFFECT OF DIFFUSIONAL CREEP ON PARTICLE MORPHOLOGY OF POLYCRYSTALLINE ALLOYS STRENGTHENED BY SECOND-PHASE PARTICLES		5. Report Date March 1973
		6. Performing Organization Code
7. Author(s) John D. Whittenberger and Donald R. Behrendt		8. Performing Organization Report No. E-7248
9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135		10. Work Unit No. 502-21
		11. Contract or Grant No.
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		13. Type of Report and Period Covered Techanical Note
		14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

Diffusional creep in a polycrystalline alloy containing second-phase particles can disrupt the particle morphology. For alloys which depend on the particle distribution for strength, changes in the particle morphology can affect the mechanical properties. Recent observations of diffusional creep in alloys containing soluble particles (γ'-strengthened Ni-base alloys) and inert particles have been reexamined in light of the basic mechanisms of diffusional creep, and a generalized model of this effect is proposed. The model indicates that diffusional creep will generally result in particle-free regions in the vicinity of grain boundaries serving as net vacancy sources. The factors which control the changes in second-phase morphology have been identified, and methods of reducing the effects of diffusional creep are suggested.

17. Key Words (Suggested by Author(s)) Diffusion; Diffusional creep; Creep; Superalloys; Dispersion-strengthened alloys; Nickel-base alloys	18. Distribution Statement Unclassified - unlimited		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 17	22. Price* $3.00

CONTENTS

EFFECT OF DIFFUSIONAL CREEP ON PARTICLE MORPHOLOGY
OF POLYCRYSTALLINE ALLOYS STRENGTHENED
BY SECOND-PHASE PARTICLES

by John D. Whittenberger and Donald R. Behrendt

Lewis Research Center

SUMMARY

Diffusional creep in a polycrystalline alloy containing second-phase particles can disrupt the particle morphology. For alloys which depend on the particle distribution for strength, changes in the particle morphology can affect the mechanical properties. Recent observations of diffusional creep in alloys containing soluble particles (γ'-strengthened Ni-base alloys) and inert particles (dispersion-strengthened alloys) have been reexamined in light of the basic mechanisms of diffusional creep, and a generalized model to explain these effects is proposed. This model predicts that diffusional creep will result in particle-free regions in the vicinity of those grain boundaries which serve as net vacancy sources. Thus, for a two-phase alloy in tension, diffusional creep will, in most cases, produce particle-free regions around those grain boundaries which tend to be normal to the applied tensile stress. According to the proposed model the factors which control the changes in second-phase morphology during diffusional creep are the inertness of the particles and the diffusion path.

The proposed model is used as a basis to predict methods of reducing the microstructural damage caused by diffusional creep. Such damage can be reduced if the grain size is increased, the diffusion coefficient is decreased, and/or the effectiveness of grain boundaries as vacancy sinks or sources is reduced.

INTRODUCTION

Several articles (refs. 1 to 7) have reported significant changes in the morphology of second-phase particles in polycrystalline two-phase alloys as a result of high temperature ($T/T_M > 0.6$) creep. In each case, denuded zones (i.e., zones free of either

dispersoids or precipitates) were observed in the vicinity of some grain boundaries. These denuded zones have been generally attributed to the effects of diffusional creep. But the exact mechanism for their formation has not been clearly defined. Several mechanisms have been proposed, but none of these apply to all the reported observations.

This report develops a generalized model which helps to explain the diffusional creep phenomenon in all the reported observations. The model is developed through application of the basic concepts of diffusional creep to alloy systems containing discrete particles. The proposed model is then used to identify those factors which control microstructural and compositional changes during creep and to predict the general effects of diffusional creep in two-phase alloys. Possible means for reducing the detrimental effects of diffusional creep are also suggested.

PROPOSED MODEL

General Description of Diffusional Creep

For close-packed alloys, substitutional diffusion occurs by a vacancy mechanism. Herring (ref. 8) in his study of diffusional creep has shown that an applied stress will affect the local concentrations of defects such as vacancies. For example, in a single-phase polycrystalline material subjected to shear, the vacancy concentration will be greater than the unstressed equilibrium value near those grain boundaries which are normal to the local tensile axis and will be lower near those grain boundaries which are normal to the local compressive axis. This produces a gradient in the vacancy concentration which results in vacancy diffusion from grain boundaries of high normal tension to those of low normal tension. Here, the normal tension is determined by the component of the local tension axis which is normal to the grain boundary. Thus, the grain boundaries of high normal tension act as net sources of vacancies, and the grain boundaries of low normal tension act as net vacancy sinks.

Since a grain boundary can be considered to be a collection of dislocations, the actual vacancy sources and sinks in grain boundaries can be viewed as jogs on these dislocations. If the jog climbs in one direction, a vacancy is produced, as shown in figure 1. If it climbs in the other direction, a vacancy is absorbed. As a vacancy source operates, it absorbs matter that is, for the dislocation shown in figure 1, the extra half plane extends. In a similar manner, as a vacancy sink operates, it must lose matter. Thus, a grain boundary can act as a source or sink for vacancies. Furthermore, when a grain boundary acts as a vacancy source, it must absorb mass; and when

a boundary acts as a vacancy sink, the boundary must lose mass.

When a vacancy is created at one location, moved, and annihilated at a second location, the net effect is to move an atom in the reverse direction. Therefore, atoms are deposited at grain boundaries of high normal tension (vacancy sources), and atoms are removed from grain boundaries of low normal tension (vacancy sinks). Such movement of mass produces creep, and the material in question elongates in the direction of tension.

Development of General Model

We now consider diffusional creep in a two-phase system consisting of discrete particles embedded in a matrix. Since atoms are being deposited at grain boundaries of high normal tension, the atoms (lattice sites) originally next to these grain boundaries are moved away from the boundaries. In a like manner, any markers embedded in the crystal next to the boundaries would be moved away from the boundaries. The markers could be, for example, small inclusions or precipitate particles. Thus, an alloy initially containing a uniform distribution of particles, after experiencing a sufficient amount of diffusional creep, can exhibit bands which are denuded of particles. In this case, each band would contain a grain boundary which acted as a source of vacancies during creep. Also, near the grain boundaries which act as sinks for vacancies, lattice sites would be moved toward these grain boundaries. Markers (particles) embedded in the matrix near these grain boundaries would also be moved toward these boundaries. During continued diffusional creep the particles would be moved closer to and eventually would encounter the grain boundaries serving as vacancy sinks. What happens to the particles as they encounter the grain boundary depends on their degree of inertness and on the vacancy diffusion path.

We shall consider four cases: (1) inert particles and diffusion by bulk vacancy diffusion, (2) inert particles and diffusion by grain boundary vacancy diffusion, (3) noninert particles and diffusion by bulk vacancy diffusion, and (4) noninert particles and diffusion by grain boundary vacancy diffusion. We apply the term inert or noninert to a particle depending on its behavior when it is in contact with a grain boundary serving as a vacancy sink. If, as vacancies are annihilated at the region of contact between the particle and grain boundary, atoms of the particle are removed from the particle and diffuse away, the particle is defined as "noninert." On the other hand, a particle is defined as "inert" if either (1) vacancies are not annihilated at the continuous alloy/grain boundary/particle junctions or (2) vacancies are only annihilated on the continuous alloy/grain boundary side of such junctions. In simpler terms, inert particles cannot absorb vacancies; thus, inert particles remain intact during diffusional creep.

In the following discussion we consider alloys containing inert particles to be composed of a matrix alloy in which the discrete particles are embedded. The composition of the matrix is A, while the composition of the particles is B. We consider alloys containing noninert particles to be well annealed at the test temperature such that the effects of particle growth in the grains need not be considered; however, such particle growth during diffusional creep will not change the overall results. We consider that the noninert particles differ from the matrix at least in composition, where the matrix is the material in which the particles are embedded. Furthermore, we specify the initial composition of the matrix to be C and that of the well-annealed particles to be D. Thus, if in a given region the particles were to dissolve in the matrix to produce a homogeneous mixture, the composition of this region would be a mixture of C and D.

During diffusional creep, zones denuded of the original particles will be formed adjacent to grain boundaries of high normal tension; however, the composition of this zone may vary for the different cases. For the four cases, we now determine how the concentration of these denuded zones varies, how the particle morphology and composition change at grain boundaries of low normal tension (vacancy sinks), and how the creep rate varies with time during diffusional creep.

Alloys containing inert particles. - For inert particles and for diffusion by either bulk vacancy or grain boundary vacancy diffusion, cases 1 and 2, the results are the same. Denuded zones are formed around grain boundaries of high normal tension (the vacancy sources), and the composition of these zones is A because of the inertness of the particles. Also, the particles should collect about the grain boundaries of low normal tension (the vacancy sinks), increasing the concentration of particles adjacent to these grain boundaries compared to their concentration in the interior of the grain. This behavior is shown schematically in figure 2. Provided that the grain boundaries serving as vacancy sinks cannot move over the surface of the particles, these grain boundaries become increasingly less efficient as vacancy sinks as more and more particles encounter the grain boundary. Finally, the particles completely block operation of these vacancy sinks. This then leads to a diffusional creep rate which decreases with time during creep. If, however, the grain boundaries can move over the particle surfaces, or if other vacancy sinks such as internal surfaces (voids or cracks) become active because of the increased vacancy concentration near the vacancy sources, the creep rate may increase with time.

Alloys containing noninert particles. - We now consider case 3: noninert particles with bulk vacancy diffusion. As the particles encounter the grain boundaries serving as vacancy sinks, the particles can dissolve (i.e., they absorb vacancies). Thus, the matrix near these sinks no longer has composition C, but is a mixture of C plus D. Since the matrix concentration is displaced from the near equilibrium concentration C, the particles in the vicinity of the vacancy sinks can grow. If the bulk diffusion rate is

4

slow compared to the growth rate, the region of particle growth will be confined to those particles adjacent to the vacancy sinks. Because of the particle growth, the flux of mass necessary to compensate for the vacancy flux will be of composition C. Thus, the denuded zones formed at the grain boundaries serving as vacancy sources will be of composition C, the matrix composition. Finally, because the particles do not have a blocking effect at the vacancy sinks, as was the case for inert particles (cases 1 and 2), the diffusional creep rate should remain constant with time.

Lastly, we consider case 4: noninert particles and diffusion by grain boundary diffusion. In this case, particles can dissolve as they encounter the grain boundaries serving as vacancy sinks. Thus, the composition of the atom flux flowing along grain boundaries to the vacancy sources will be some mixture of C and D. As the flux moves toward the vacancy sources, there will be a tendency for the elements normally segregated to the particles to reattach themselves on particles lying in the diffusion path. Such behavior will tend to increase the size of particles touching the vacancy sinks. This in turn increases the amount of material of composition D going into solution because the overall contact area of particle/grain boundary junctions has increased. Eventually a steady state will be reached between the size of the particles and the composition of the atom flux flowing to the vacancy sources. If both the matrix/grain boundary and particle/grain boundary junctions can serve as equally good vacancy sinks (particles are truly noninert), the average size of the particles along the grain boundaries serving as the vacancy sinks will be equivalent to the average size of the particles in the grain interior. If, on the other hand, particle/grain boundary junctions are not as good vacancy sinks as are the matrix/grain boundary junctions (i.e., the particles exhibit semiinert behavior), the average size of the particles along the grain boundaries serving as vacancy sinks will be larger than the average size of the particles in the grain interior. Thus, for this example, the local volume fraction of particles will be larger around the vacancy sinks than in the interior of the grains. For either of these examples at steady state, the composition of the atom flux to the vacancy sources will be equal to the overall alloy composition: $DX + C(1 - X)$, where X is the fraction of particles in the alloy. Thus, the composition of the denuded zones will approach the overall alloy composition as diffusional creep proceeds. These denuded zones will consist of a single phase if nucleation of second-phase particles is difficult. On the other hand, if nucleation sites are available, precipitation and growth of second-phase particles can occur in the ''denuded'' zones. In general, the morphology of these precipitated particles will be different from the morphology of particles in the grain interior.

Model summary. - The results for the four cases are summarized in table I.

DISCUSSION

Prior Work

Dispersion-strengthened alloys. - Several observations of diffusional creep have been reported for various materials containing inert particles. For example, diffusional creep has been observed during elevated temperature ($T/T_M \approx 0.8$) creep and slow tension testing of hydrided Mg-Zr alloys (refs. 1 to 4). The alloys tested were nominally Mg-0.5Zr, which formed a dispersion of ZrH_2 particles when annealed in hydrogen. During testing, ZrH_2-free regions were formed around those grain boundaries which tended to be normal to the applied tensile stress. This observation was interpreted as evidence that diffusional creep occurred. In addition, recent work at the NASA Lewis Research Center (ref. 5) has shown that TD-NiCr (Ni-20Cr-2ThO$_2$) undergoes diffusional creep during slow strain rate, high temperature testing. Metallographic examination of tested specimens revealed whitish-gray bands in the vicinity of grain boundaries. Electron microprobe analysis showed that the chromium concentration in the bands and matrix was similar; however, the thorium concentration in the bands was much lower than in the matrix. The thorium concentration results indicated that the bands contained few, if any, ThO_2 particles. This was confirmed by electron replica metallography. It was concluded that these bands were the result of diffusional creep where the grain boundary within each band acted as a net vacancy source.

These results (refs. 1 to 5) concerning diffusional creep in systems believed to contain inert particles are consistent with either case 1 or case 2 of the proposed model. Particle-free regions were observed in the vicinity of certain grain boundaries in both TD-NiCr and Mg-ZrH$_2$ alloys. In addition, one study (ref. 4) observed regions of apparent particle agglomeration. Possibly, regions of particle agglomeration were not observed in the other studies because these regions do not provide as definite metallographic contrast with the bulk alloy as do the denuded zones. Because these studies generally did not involve measurement of the creep rate, little can be said about possible changes of creep rate with time for these materials. However, in a similar study of diffusional creep polycrystalline copper containing alumina particles, Burton (ref. 9) observed that the creep rate decreased with time during the creep test. He proposed that this decrease was caused by the inability of regions of grain boundaries in contact with alumina particles to function as vacancy sinks. As the creep test proceeded, the density of alumina particles on the grain boundaries serving as vacancy sinks would be continuously increasing, and thus the overall efficiency of these boundaries as vacancy sinks would be continuously decreasing. If the alumina particles are considered to be inert in the sense used herein, either case 1 or case 2 applies to Burton's observations for the decreasing creep rate.

<u>Precipitation-strengthened alloys</u>. - Two recent articles (refs. 6 and 7) have indicated that diffusional creep is an active mechanism during high-temperature $(T/T_M > 0.6)$ creep of γ'-strengthened Ni-base superalloys. In both studies, γ'-free regions were formed in the vicinity of grain boundaries which tended to be normal to the applied tensile stress. Also, Tien and Gamble (ref. 6) observed γ' enrichment at grain boundaries which tended to be parallel to the applied tensile stress, while Gibbons (ref. 7) found a few γ' particles in the "precipitate-free" zones. To determine if composition differences existed, the crept alloys were subjected to electron microprobe analysis. After creep testing a Ni-16Cr-4Al-5Ta alloy at 1255 K, Tien and Gamble found that the γ'-free zones had high chromium levels and low aluminum and tantalum levels, while the γ'-enriched areas exhibited the opposite behavior. In addition, they found that the chromium content of the γ'-free regions was greater than that of the bulk alloy $(\gamma + \gamma')$ and that the ratio of chromium content in the γ'-denuded regions to that in the γ'-enriched regions was approximately 3. On the other hand, Gibbon's microprobe analysis of Ni-20Cr-2.5Ti-1.5Al alloys creep tested between 1023 and 1123 K showed no differences in chromium, titanium, or nickel levels between the γ'-free regions and the bulk alloy.

In terms of a physical model, Gibbons proposes that the γ'-free regions are formed by diffusional creep where sufficient diffusion of each constituent (Al, Cr, Ni, and Ti) occurred to maintain similar composition in the bulk alloy and γ'-free regions. Tien and Gamble (ref. 6) also propose that the γ'-free regions are formed by diffusional creep; however, they believe that only chromium and nickel atoms are migrating, and this results in the dissolution of γ' at grain boundaries normal to the applied tensile stress and growth of γ' at boundaries parallel to the stress (i.e., negligible migration of aluminum or tantalum atoms).

In the case of Tien and Gamble's work, we believe that their observations can be explained by the model presented herein and that they are consistent with either case 1, 2, or 3: inert particles with either bulk or grain boundary vacancy diffusion, or non-inert particles with bulk vacancy diffusion. We believe case 3 to be the most likely mechanism. This is supported by Tien and Gamble's observation that prolonged annealing at the test temperature under zero stress produces a growth in the γ' particle size. This means that the γ' particles are not inert at this temperature and that bulk diffusion was responsible for their growth since the γ' particles are in the interior of the grains. Our model then predicts (1) that zones denuded of γ' should form, surrounding grain boundaries running approximately perpendicular to the applied tension axis; (2) that clustering or growth in size of γ' particles should occur along grain boundaries running approximately parallel to the applied tension axis; and (3) that the composition of the denuded zone should be that of the matrix (γ). Tien and Gamble's micrographs show the γ'-denuded zones and the clustering or growth of the γ' particles

the appropriate grain boundaries. Their microprobe results confirm their observed microstructure since the γ-phase should be high in chromium and low in aluminum and tantalum, while the γ'-phase should be low in chromium and high in aluminum and tantalum (ref. 10). If γ' particles were dissolving at vacancy sources to form the denuded zones, as proposed by Tien and Gamble, one would expect a predominence of smaller γ' particles to outline these denuded zones. However, on examining their photomicrographs, there is no noticeable difference in the sizes of γ' particles near the γ'-free zones and those in the interior of the grain. While Tien and Gamble dissolution and growth argument cannot be ruled out on the basis of the preceding discussion, the dissolution and growth argument is not necessary to explain their observations since the formation of γ'-denuded bands and the clustering or growth of γ' at other grain boundaries is a direct and necessary result of diffusional creep.

Turning now to the results of Gibbons (ref. 7), he has indicated that a grain boundary diffusion mechanism likely makes a substantial contribution to the creep rate under the stress and temperature conditions described. Considering the γ' particle to be noninert and diffusion to be by a grain boundary mechanism, the result of our model (case 4) indicates the following: (1) the γ'-particle denuded zones should have a composition which is the same as the grain interior of the bulk alloy ($\gamma + \gamma'$), and (2) no clustering of γ' particles would occur at the vacancy sinks. Gibbons electron probe scans for Cr, Ni, and Ti of the Ni-20Cr-2.5Ti-1.5Al alloy after creep testing indicated that there was no change in the concentration of the Ni, Cr, and Ti on scanning from the grain interior through the denuded zone. In other words, the denuded zone had the same composition as the bulk alloy ($\gamma + \gamma'$). This finding is consistent only with case 4. Since a few rather large γ' particles were seen by Gibbons in the "precipitate-free" zones, the supersaturation of Al and Ti in these regions is reduced by nucleation and growth of γ' particles. Furthermore, there is a difference in the γ' morphology between the "precipitate-free" regions and the bulk alloy. This difference is probably caused by the different sets of conditions for nucleation and growth; that is, for the "precipitate-free" regions, particles formed by nucleation and growth under an applied stress at the test temperature; while for the bulk alloy, particles formed by nucleation and growth after a high temperature anneal and quenching to the test temperature. Finally, little can be said about the γ' distribution about the vacancy sinks because Gibbons' photomicrographs do not clearly delineate the microstructure around grain boundaries which are generally parallel to the applied tensile stress.

Possible Effects of Diffusional Creep

On the basis of the diffusional creep model and previous observations of diffusional creep, it is apparent that diffusional creep can affect the microstructure of two-phase

polycrystalline alloys. These changes can be particularly important when the strength of the alloy depends on the second-phase morphology. For example, diffusional creep in a two-phase alloy under tension can result in particle-free regions surrounding those grain boundaries which are generally transverse to the applied stress. Once the particle-free regions are formed, additional localized creep deformation can take place in these regions because they are usually much weaker than the bulk (two-phase) alloy. This can lead to crack (void) formation in the particle-free regions and eventually to the failure of the alloy. Such behavior has apparently been observed during elevated temperature testing of TD-NiCr (ref. 5), Ni-base alloys (refs. 7 and 11), and ZrH_2-strengthened magnesium alloys (ref. 3). The creep deformation in the denuded regions can be by creep mechanisms other than diffusional creep; however, once cracks (voids) are developed in these regions, the cracks can serve as vacancy sinks. This results in very short distances between the vacancy sources and sinks and produces very high creep rates.

Because of the reasoning outlined, the microstructural damage due to diffusional creep in two-phase alloys can be the most important effect of diffusional creep. Thus, long term, high temperature mechanical properties can be seriously influenced by microstructural changes caused by diffusional creep. Such changes will occur whenever diffusional creep can account for a portion of the overall strain; that is, diffusional creep need not be the predominate creep mechanism. This again points out some of the problems involved in extrapolating short term test data (where diffusional creep is not important and little or no microstructural damage occurs) to obtain estimates of the long term mechanical properties (where diffusional creep can contribute to the overall creep strain and particle-free regions are formed). Furthermore, diffusional creep may be a particularly important creep mechanism in alloys which purposefully contain second-phase particles to impede dislocation motion as these particles increase the range of stresses over which diffusional creep can significantly contribute to the overall defromation (ref. 12).

Under what conditions will diffusional creep contribute to the overall creep deformation? We suspect that, in general, diffusional creep will occur in most two-phase alloys whenever they are used for reasonably high temperature ($T \geq 0.5 \, T_M$), long term, low total plastic strain applications. One can easily estimate the theoretical creep rates from either grain boundary diffusion (ref. 13) or volume diffusion (ref. 8) if values for the applied stress, use temperature, grain size, appropriate diffusion coefficient, atomic volume, and grain boundary thickness are known. The calculated creep rates can then be compared to the desired rates to see if diffusional creep will contribute to the overall strain.

Control of Diffusional Creep

The basic premise of any diffusional creep model is that an applied stress can affect the local concentration of vacancies in the vicinity of grain boundaries. Specifically, grain boundaries subjected to a high normal tension stress become surrounded by a higher concentration of vacancies than grain boundaries subjected to a low normal tension stress. The vacancy concentration gradient between grain boundaries of high and low normal tension results in vacancy flow. This flow is counterbalanced by an atom flow in the opposite direction. The net result of the atom flow is the transport of mass from grain boundaries of low normal tension stress to those of high normal tension stress; this produces creep in the alloy.

In order for diffusional creep to occur continuously, the following conditions must be satisfied: (1) the alloy must be subjected to a stress, (2) grain boundaries subjected to high normal tension stresses must act as vacancy sources, (3) grain boundaries subjected to low normal tension stresses must act as vacancy sinks, and (4) diffusion of vacancies (atoms) must occur. To reduce the importance of diffusional creep, one must lower the applied stress, reduce the effectiveness of the vacancy sinks and/or sources, and/or impede vacancy (atom) diffusion. Of these methods, only the latter two offer attractive potential.

Alloy designers and users can reduce the amount of diffusion, and hence the rate of formation of particle-free regions, by increasing the length of the diffusion path and/or by decreasing the diffusion coefficient. Since the diffusional creep rate due to volume diffusion is proportional to (grain size)$^{-2}$ (ref. 8) and the creep rate due to grain boundary diffusion is proportional to (grain size)$^{-3}$ (ref. 13), increasing the grain size should reduce the diffusional creep rate and generally should reduce microstructural damage. But, in some cases, increasing the grain size will not reduce the formation rate of particle-free regions. For example, in thin sheet materials under tension the sheet surfaces, as well as grain boundaries of low normal tension, can act as vacancy sinks. Therefore, increasing the grain size such that it is greater than the sheet thickness cannot reduce the rate of formation of particle-free regions because the maximum distance between the vacancy sources and sinks will always be about one-half the sheet thickness.

The other method to reduce the amount of diffusion is to decrease the vacancy (atom) diffusion coefficient. If volume diffusion is rate controlling, reasonable reductions (an order of magnitude or more) in the diffusion coefficient may require either large changes in the chemistry of the matrix (continuous alloy phase) or substitution of a higher melting element or phase as the matrix. While these options are generally plausible for dispersion-strengthened alloys, they have very limited application for precipitation-hardened alloys. On the other hand, if grain boundary diffusion is rate controlling, it

may be possible to effectively reduce the diffusion coefficient by small alloying additions which affect the grain boundaries (refs. 14 and 15). Apparently, the addition of small amounts of B and Zr to γ'-strengthened Ni-base alloys reduces creep in this manner (ref. 14).

The most direct method for preventing the formation of particle-free bands would be to prevent the operation of vacancy sinks and/or sources. Experimentally, it has been shown (refs. 5, 9, and 16) that a threshold stress for diffusional creep exists for several polycrystalline alloys containing a dispersed second phase. That is, in order for creep to occur, the applied stress must exceed the threshold stress. Such behavior is generally interpreted as the inability of grain boundaries to act as perfect sinks or sources (ref. 16). Burton (ref. 9) has shown, for diffusional creep in copper containing alumina particles, that the threshold stress depends on the test temperature and on the volume fraction of alumina particles. Also factors such as particle solubility, particle distribution on the grain boundaries, prior thermomechanical processing, chemistry of the grain boundaries, and grain size must also influence the magnitude of the threshold stress. Unfortunately, the specific effects on these variables on the threshold stress is not known. Certainly, further experimentation and theoretical work is required in this area.

CONCLUSIONS

The proposed model of diffusional creep in two-phase alloys can account for the changes in microstructure observed during creep. In general, diffusional creep in a polycrystalline alloy containing discrete second-phase particles will result in particle-free regions surrounding those grain boundaires which act as vacancy sources. Thus, for a two-phase alloy in tension, diffusional creep will produce particle-free regions around those grain boundaries which tend to be normal to the applied stress. Such changes in the microstructure can be particularly important if the strength of the alloy depends on the second-phase morphology.

The proposed model is used as a basis to predict methods of reducing the microstructural damage caused by diffusional creep in two-phase alloys. Such damage can be reduced if the grain size is increased, the diffusion coefficient is decreased, and/or the effectiveness of the grain boundaries as vacancy sinks or sources is reduced.

Lewis Research Center,
    National Aeronautics and Space Administration,
        Cleveland, Ohio, November 27, 1972,
            502-21.

REFERENCES

1. Squires, R. L.; Weiner, R. T.; and Phillips, M.: Grain-Boundary Denuded Zones in a Magnesium-1/2 wt% Zirconium Alloy. J. Nucl. Mat., vol. 8, no. 1, Jan./Feb. 1963, pp. 77-80.

2. Karim, Anivar-ul; Holt, David L.; and Backofen, Walter A.: Diffusional Creep and Superplasticity in a Mg-6Zn-0.5Zr Alloy. Trans. AIME, vol. 245, no. 5, May 1969, pp. 1131-1132.

3. Karim, Anwar-ul; Holt, David L.; and Backofen, Walter A.: Diffusional Flow in a Hydrided Mg-0.5 Wt pct Zr Alloy. Trans. AIME, vol. 245, no. 11, Nov. 1969, pp. 2421-2424.

4. Rainey, P. E.; and Holt, D. L.: An Observation by Transmission Electron Microscopy of Diffusional Creep in a Magnesium Alloy. Met. Trans., vol. 2, no. 11, Nov. 1971, pp. 3238-3239.

5. Whittenberger, J. D.: Diffusional Creep and Creep Degradation in the Dispersion Strengthened Alloy TD-NiCr. NASA TN-7079, 1972.

6. Tien, J. K.; and Gamble, R. P.: The Influence of Applied Stress and Stress Sense on Grain Boundary Precipitate Morphology in a Nickel-Base Superalloy During Creep. Met. Trans., vol. 2, no. 6, June 1971, pp. 1663-1667.

7. Gibbons, T. B.: The Influence of Diffusion Creep on Precipitate-Free Zone Formation in Ni-20%Cr-Base Alloys. Met. Sci. J., vol. 6, Jan. 1972, pp. 13-16.

8. Herring, Conyers: Diffusional Viscosity of a Polycrystalline Solid. J. Appl. Phys., vol. 21, no. 5, May 1950, pp. 437-445.

9. Burton, B.: The Influence of Alumina Dispersions of the Diffusion-Creep Behavior of Polycrystalline Copper. Met. Sci. J., vol. 5, Jan. 1971, pp. 11-14.

10. Kriege, Owen H.; and Baris, J. M.: The Chemical Partitioning of Elements in Gamma Prime Separated from Precipitation-Hardened, High-Temperature Nickel-Base Alloys. Trans. ASM, vol. 62, no. 1, Mar. 1969, pp. 195-200.

11. Decker, R. F.; and Freeman, J. W.: The Mechanism of Beneficial Effects of Boron and Zirconium on Creep Properties of a Complex Heat-Resistant Alloy. Trans. AIME, vol. 218, no. 2, Apr. 1960, pp. 277-285.

12. Ashby, M. F.: A First Report on Deformation-Mechanism Maps. Acta Met., vol. 20, no. 7, July 1972, pp. 887-897.

13. Coble, R. L.: A Model for Boundary Diffusion Controlled Creep in Polycrystalline Materials. J. Appl. Phys., vol. 34, no. 6, June 1963, pp. 1679-1682.

14. D'Heurle, F. M.: The Effect of Copper Additions on Electromigration in Aluminum Thin Films. Met. Trans., vol. 2, no. 3, Mar. 1971, pp. 683-689.

15. Decker, R. F.: Strengthening Mechanisms in Nickel-Base Superalloys. Paper presented at Climax Molybdenum Company Steel Strengthening Mechanisms Symposium, Zurich, Switzerland, May 5-6, 1969.

16. Ashby, M. F.: On Interface-Reaction Control of Nabarro-Herring Creep and Sintering. Scripta Met., vol. 3, no. 11, 1969, pp. 837-842.

TABLE I. - EFFECTS OF DIFFUSIONAL CREEP IN POLYCRYSTALLINE TWO-PHASE ALLOYS CONTAINING DISCRETE PARTICLES

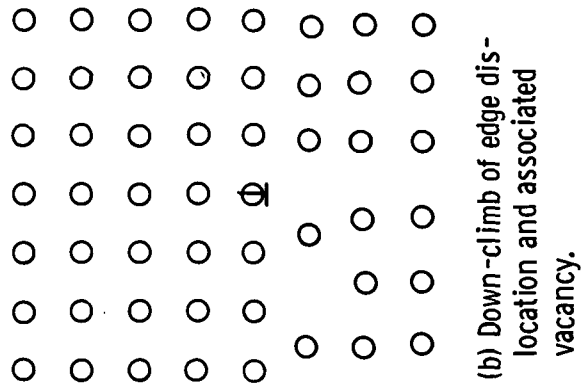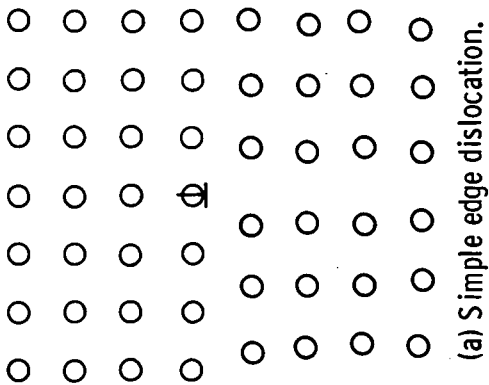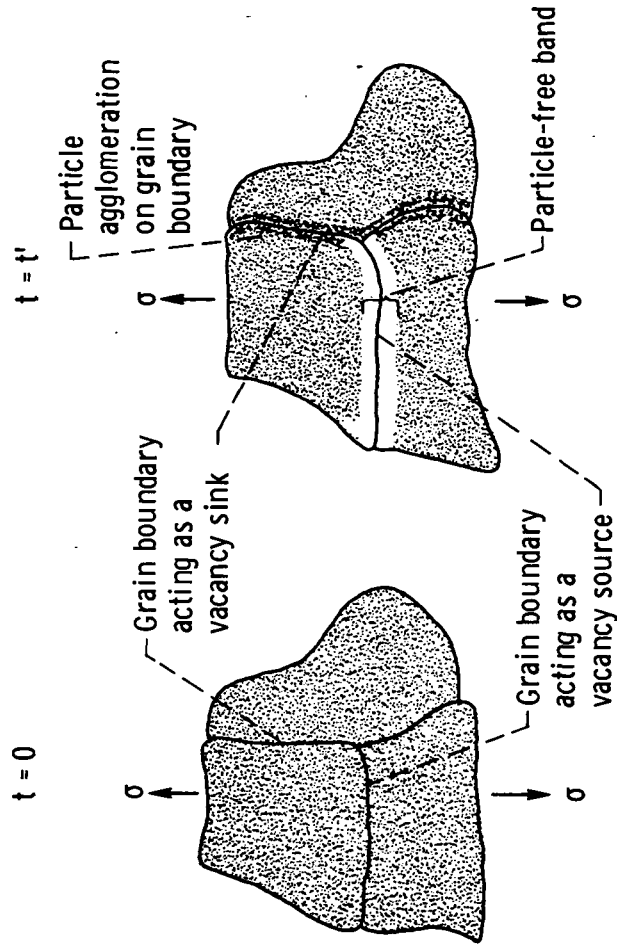| Case	Behavior of second-phase particle	Type of vacancy diffusion	Effects at grain boundaries serving as vacancy sources		Effects at grain boundaries serving as vacancy sinks		Time dependency of creep rate
			Microstructure	Composition	Microstructure	Composition	
1	Inert	Volume diffusion	Denuded regions	Same as original matrix (continuous phase)	Clustering of particles; particles near sinks; sintering of clusters possible	Approaches that of particles	Decreases with time unless other sink become active
2	Inert	Grain boundary diffusion					
3	Noninert	Volume diffusion	Denuded regions	Same as original matrix	Growth of particles near vacancy sinks	Approaches that of particles	Constant with time
4	Noninert	Grain boundary diffusion	"Denuded" regions which may contain second-phase particles if nucleation is favorable	Approaches original alloy composition (matrix plus particles)	Same as grain interior	Same as original alloy composition	Constant with time

14

Figure 2. – Schematic representation of particle-free band and particle agglomeration formed during diffusional creep in a polycrystalline alloy containing inert particles.

t = 0

t = t'

Particle agglomeration on grain boundary

Particle-free band

Grain boundary acting as a vacancy sink

Grain boundary acting as a vacancy source

σ   σ

σ   σ

(a) Simple edge dislocation.

(b) Down-climb of edge dis-location and associated vacancy.

Figure 1. – The edge dislocation operating as vacancy source.

"*The aeronautical and space activities of the United States shall be
conducted so as to contribute . . . to the expansion of human knowl-
edge of phenomena in the atmosphere and space. The Administration
shall provide for the widest practicable and appropriate dissemination
of information concerning its activities and the results thereof.*"
—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons. Also includes conference proceedings with either limited or unlimited distribution.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include final reports of major projects, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION OFFICE

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D.C. 20546